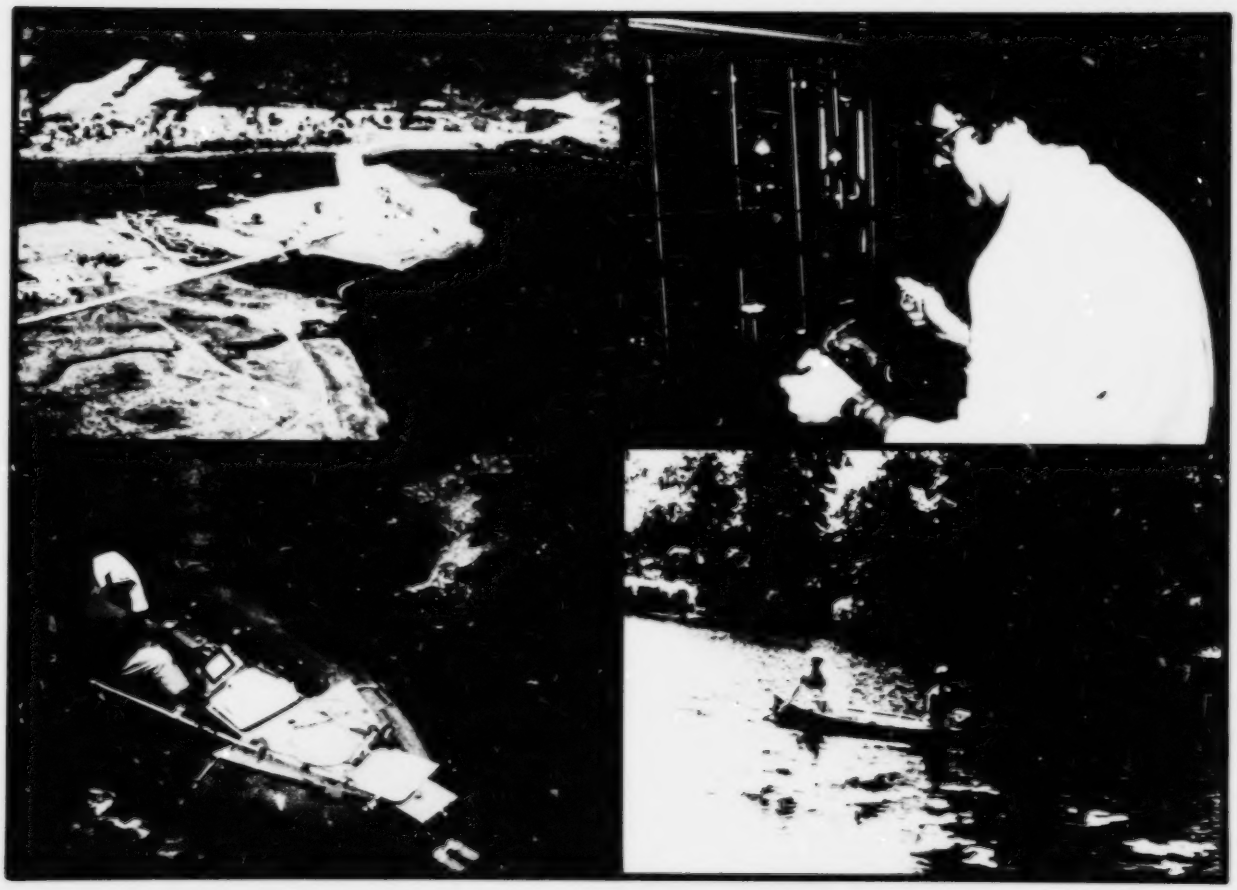
Environment Canada Environnement Canada

WATER QUALITY BRANCH ATLANTIC REGION FIELD QUALITY ASSURANCE/QUALITY CONTROL PROGRAM. VERSION 2

IW/L—AR—WQB—87—126



Canada

INLAND WATERS DIRECTORATE
ATLANTIC REGION
WATER QUALITY BRANCH
MONCTON, NEW BRUNSWICK

WATER QUALITY BRANCH ATLANTIC REGION
FIELD QUALITY ASSURANCE/QUALITY CONTROL PROGRAM.
VERSION 2

IW/L-AR-WQB-87-126

INLAND WATERS/LANDS DIRECTORATE
CONSERVATION AND PROTECTION
ENVIRONMENT CANADA

Richard A. Arseneault
Geoffery D. Howell

Water Quality Branch
Atlantic Region
Moncton, New Brunswick
Feb. 9, 1987

A copy will be made available in French upon request

TABLE OF CONTENTS

	PAGE
Abstract	ii
Résumé	ii
Acknowledgements	iii
Introduction	1
Discussion	8
1. A Few Words on Work Planning and Analytical Laboratory Aspects	8
2. Field Trip Preparation	13
3. Water Quality Sampling and Field Analysis	14
3.1 Training of Personnel	14
3.2 Sampling Procedures - General	15
3.3 Sampling Equipment	19
3.4 Sample Bottles	20
3.5 Field Analysis: Field Meters and Meter Calibration	23
3.6 Field Analysis: General	24
3.7 Field Record Keeping	26
3.8 Sequential Triplicate Sampling	27
3.9 Sample Preservation, Filtration, Handling and Storage	30
4. Sampling for Toxic Chemicals	35
4.1 Water	36
4.2 Bottom Sediments	45
4.3 Biota	51
5. Recommendations	54
References	59

ABSTRACT

The present report explains in detail the various components of the Water Quality Branch, Atlantic Region field quality assurance/quality control program. It covers the routine monitoring activities and the more complex toxic chemical surveys. Water, bottom sediments and biota sampling protocols are presented, with special emphasis on specific field QA/QC procedures employed. Recommendations are made to explore and/or improve certain QA/QC aspects of toxic chemical sampling.

RÉSUMÉ

Le présent rapport explique en détails les diverses composantes du programme d'assurance et de contrôle de la qualité de la Direction de la qualité des eaux, région de l'Atlantique, en ce qui concerne le travail effectué sur le terrain. Les exigences des activités routinières de relevés ainsi que celles des études plus complexes sur les substances toxiques sont élaborées dans ce document. Les protocoles d'échantillonnage de l'eau, des sédiments de fond et du biota sont présentés, avec une emphase marquée sur les procédures spécifiques d'assurance et de contrôle de la qualité employées sur le terrain. Des recommendations sont faites pour explorer et/ou améliorer certains aspects touchant à l'assurance et au contrôle de la qualité en rapport avec l'échantillonnage des substances chimiques toxiques.

ACKNOWLEDGEMENTS

The authors would like to thank all the staff at the Water Quality Branch, in Moncton. Special thanks to Louise Boulter for typing this manuscript. The authors are particularly grateful to D.H. Cullen, H.J. O'Neill, G.L. Brun, L. Desilets, Dr. J.E. Gaskin and Dr. T.L. Pollock for reviewing this manuscript.

INTRODUCTION

Numerous studies such as those conducted at Hubbard Brook have indicated that 5 to 20 years of baseline water quality data may be necessary to adequately characterize the complexity of ecological interactions and systems (Likens, 1980). This lack of high quality long term monitoring data has hindered the elucidation of the effects of recent environmental issues such as LRTAP and toxic chemicals. Therefore, future water quality monitoring programs must be designed such that they provide high quality, consistent data in order to assist in addressing both current and future environmental problems.

With this in mind, the Water Quality Branch, Atlantic Region (WQB-AR), reviewed historical data sets and identified an urgent need for improvement of field quality assurance/quality control (QA/QC) procedures. Starting in April 1984, a new consistent field QA/QC program was instituted for all WQB-AR projects. This program was described in detail in a draft report (Arseneault et al., 1984) and will be revised in this updated version. In addition, the present report includes a whole section on field QA/QC procedures used specifically for trace toxic organic chemical determinations.

Note that, in this document, what is called "field QA/QC program" deals with all QA/QC activities accomplished in the field, by field personnel. However, field and lab QA/QC activities are not only complementary, but in many ways, are interdependent (Chau

and Lawrence, 1984) to obtain a final product (data) of a known level of quality. Therefore, in this document, some lab QA/QC aspects will also be touched upon to complement the discussion.

A good QA/QC program is essential in supporting the credibility (King, 1982) of data generated through water quality studies. This is true for all water quality monitoring and survey activities, especially when the object of the work is the measurement, and subsequent interpretation of trace contaminants in various types of sample matrices (clear water, turbid water, bottom sediments, fish tissues, ...).

Analyzing for trace organic contaminants is generally time consuming and costly. It requires multi-step procedures (preservation, extraction, clean-up, ...) and complex analytical instrumentation, such as gas chromatographs and high performance liquid chromatographs, which in turn require very well trained and skilled lab personnel for optimal operation. Since these analyses are performed routinely at the part-per-trillion (and lower) level, any slight contamination can pose an interference problem within the analytical process. One can realize the importance of having a number of field and lab supportive QA/QC samples (blanks, spiked blanks, replicates ...) to ascertain the integrity of actual samples. However, evaluation of the quality of the data remains something very relative (and somewhat subjective) because what can be accepted as having a high degree of quality in one case may represent a level of unacceptable quality in another.

A certain level of QA activity is needed at all times, however, the percentage of QA support should probably increase with the complexity of the measurements required. What is needed is a QA/QC program that will provide enough supportive evidence (data) to remove the doubts that data users may have when scrutinizing an overall data base.

A QA/QC program calls for QA/QC samples and related data, which can be assessed and in turn, used to document the strengths and weaknesses of data collection activities. If the need exists, improvements to the QA/QC program and rectification of some procedural shortcoming(s) can then be made. Furthermore, with such a program, it will be possible to ascribe confidence limits to the data and use this information when preparing any interpretive output. Inconsistent QA/QC results may be due to an uncontrollable natural situation, but this too would be useful information. If a QA/QC program can provide this type of information, it will have served a major part of its purpose.

Before proceeding further, it is necessary to make a distinction between the two terms, "quality assurance" (a management function) and "quality control" (an operational function):

Quality Assurance: A management function which mainly rests on the documentation and establishment of quality control protocols, and on evaluation and summarization of their outcomes (quality assessment). It is an integral part of all sampling programs and must be directed towards all aspects of monitoring including:

- network design
- station selection
- sampling (frequency, technique, ...)
- analysis (field and lab)
- data management

Quality Control: A technical, operational function which investigates and confirms the proper conduct of all those procedural components necessary for a successful conclusion. It is a system of routine checks and procedures, carried out by field, laboratory and data management personnel as part of the normal operation to ensure that the data collected meet prescribed performance standards.

Obviously, a QA/QC program will demand resources, both time and financial. What is needed is an optimal acceptable level of QA/QC activities in relation to the economics and the end result required.

In the Atlantic Region, various field QA/QC protocols have existed for many years, few of which are documented (Lockerbie, 1981). However, before 1984, no consistent field QA/QC program was ever followed on a routine basis by all field personnel in all projects, and thus, no consistent QA/QC data base really exist to show the overall degree of quality of the Atlantic Region's water data. With this in mind, WQB-AR staff decided to act quickly and, instead of wasting one or two years (or more!) on theoretical considerations for determining what should be the optimal level of QA/QC effort, they designed a field QA/QC program to provide the Branch with a preliminary evaluation of its credibility as data producer and user.

The major component of this field QA/QC program, other than documenting the proper field procedures and techniques employed, is that sequential triplicate sampling is done for at least 15% of all samples (this percentage can be as high as 20% for certain projects using non-WQB sample collectors). In addition, sample filtration, preservation and blank preparation are carried out at the end of the sampling day, instead of being done at each sampling site (or other). Further explanations concerning these procedures will be given later in this report.

Sequential triplicate sampling is an important part of our field QA/QC program, and also touches some lab and data management QA/QC aspects. Data originating from this triplicate sampling program are produced by the lab and they can be used as checks on

the analyses performed. However, this program was not initially intended to be used in this fashion. In other words, no more effort should be spent by the lab on these triplicate samples than that spent for any other regular sample submitted for analysis. As previously stated, the analytical laboratory has a QA/QC program of its own. All data generated by it are validated through ionic balances, comparison with historical data. ... Individual sequential triplicate samples are also validated in this way.

Preliminary sequential triplicate data analysis was done (Arseneault and Howell, 1985) and provided very useful information concerning the data variability observed for some water quality parameters. However, when the preliminary data analysis was carried out, the sequential triplicate data base was relatively small, and thus, no statistical significance could be ascribed to the observations. Presently, a thorough field QA/QC data evaluation is being performed and will be appropriately documented in future reports.

The WQB presently has a field manual (WQB, 1983) which covers a good portion of the material in this report. Also, a national WQB document on QA/QC guidelines and principles covering lab, field and data management aspects is in preparation. However, the present document is intended to be of a more specific nature in order to meet the needs of the Atlantic Region field programs.

Historically, the WQB was more lab than field oriented and thus, numerous lab QA/QC procedures (interlab and intralab) are in place. Many QA/QC procedures have resulted from participation in national programs, such as LRTAP (Work Group on Quality Control, 1983; Brun, 1986), which require stringent QA/QC protocols. Thus, it is safe to say that the Analytical Services Division presently has a well oiled QA/QC program. Presently, the measurement uncertainties associated with the field sampling and measurement steps of water quality data collection process far outweigh the uncertainties associated with the analytical laboratory aspects of the process. The development of an overall quality assurance program for the WQB requires that all steps in the data collection process be in control, and that is why we have been striving to improve our field QA/QC program since 1984.

This present document will require regular updates to reflect the evolution of our field QA/QC program, and to document new sampling techniques and protocols that may be put in place in the future. One area that the WQB-AR is not presently involved in, regarding toxic chemicals, is the bioassay environmental sensing (ecotoxicological) approach (Blaise et al., 1985; Ongley et al., 1986). If this type of activity is adopted by the WQB-AR in the future, proper field and lab QA/QC protocols will have to be developed, tested and documented.

DISCUSSION

1. A Few Words on Work Planning and Analytical Laboratory Aspects

Prior to commencing any water quality monitoring or survey projects, proper planning (study design, work schedules, resources, ...) must be done to address all questions and issues of interest to the study. Some of WQB-AR work is related to monitoring river water quality at international boundaries and comparing the related data with water quality objectives (ITAS, 1980; Howell, 1984, Lockerbie, 1987). In another case, the project is designed to study the degree to which acid precipitation is affecting the lakes in this region (Howell, 1986). Appropriate planning of these projects was done, with judicious sampling site selection, sampling frequency, parameter list and QA/QC protocols.

The planning process constitutes the basis of the region's monitoring and survey projects. Planning is a year to year concern and is influenced by results obtained during the previous year(s) of work. In other words, planning and yearly data scrutiny do go hand in hand, where applicable. In addition, preliminary field work is often required a year in advance to help finalize the planning of any given study. The same approach is applied to the lab activities, where analytical method modification and/or development may be required for a new project to start.

In the case of the toxic chemical survey projects, the main concerns (issues) in the Atlantic Region are pesticides used for agricultural and forestry purposes, some industrial and mining activities and the long range transport of atmospheric toxic chemical pollutants. Historically, this program was mainly aimed at screening for priority pollutants in the whole Atlantic Region (Bailey, 1984; Bailey, 1985). However, in recent years, the WQB-AR has been working on a smaller scale (Clair et al., 1987) with more specific objectives in mind, and this approach will surely continue in the future. Some screening work still continues, and the Federal/Provincial Agreement(s) have adopted this approach, on a yearly basis, to ascertain the long term trends exhibited by some pollutants (mainly OC-PCB's) in this region.

The key to success in the toxic chemical survey projects is planning. Planning has been inadequate in the past, mainly because the monitoring of toxic chemicals (principally the organics) from a water quality perspective is relatively new in the region. However, the experience gained during that period of time will serve us in the future.

One approach for toxic chemical projects in the next few years, will be to concentrate the field work on a smaller lake, pond or stream situated in a region where toxic chemicals of interest are known to be used. More samples (both spatial and temporal) could then be collected in a given area, to furnish a more representative picture of the whole situation and, also, to

provide more statistically sound results for data interpretation.

For example, it could be a small lake located in an agricultural area receiving known amounts of pesticides, in which sampling of various media could be made before, during and after pesticide applications on the agricultural field. A biological monitoring tool such as changes in structure within benthic invertebrate communities or some type of bioassay tests may be added to the study in order to provide some biological information in addition to the chemical measurements made. Flow data from the exit stream will be needed to evaluate water renewal rates in the lake, during the study period. Sampling prior to, during and after rain events may be required. In addition, general water chemistry characteristics will be monitored during the study. A thorough field QA/QC program, as explained later in this manual, will be followed.

Some of the toxic chemical QA/QC data produced in the past were used as a starting basis to formulate proper recommendations in terms of new improved field QA/QC protocols (given later in this text). Also, some guidelines on this aspect of the work, as presented in the scientific literature (ACS Committee, 1980; 1983; Taylor and Stanley, 1985) were followed. Obviously, a good knowledge of the toxic chemical(s) of concern is required, which means conducting a complete literature search prior to the planning of any study. There may also be some cooperation between the WQB and other federal or provincial agencies in the planning and doing

of the work. The history of previous pesticide applications in the study area will also be required.

Work planning should be a group effort rather than a strictly individual effort. Obviously, a project leader must continue to plan the work of his section for the coming year. However, it is suggested that other project leaders should have a chance to critically review the plans whenever this is possible. A meeting should then be arranged to optimize all project plans. There is also the question of optimization of the field QA/QC aspects of the work and coordination of this with the analytical laboratory people.

All lab methodologies should be well documented, and this information should be made available to the project scientist. Also, all lab QA/QC results should continue to be made available to the project scientist. It is recommended that these results should be entered in the computer registry. Proper coding is needed for easy retrieval.

In the Atlantic Region, the WQB lab follows analytical methods documented in the "Analytical Methods Manual" (WQB, 1981). New analytical methods developed will also be documented in future updates of this manual. Summary description of all methods are given in the "NAQUADAT Dictionary of Parameter Codes" (WQB, 1986). Any changes in lab methodology should be documented appropriately and the project scientist should be made aware of these changes, as

soon as possible. If interlab QC exist, the results of this exercise should be made available to the project scientist.

In terms of lab data management, the Atlantic Region Water Quality lab is using the LABS-11 laboratory data management system (WQB-AR, 1982; Wong et al., 1984). This software has provisions for many sample validation checks. In addition, a number of lab (and field) QC-PE (quality control - performance evaluation) data checks are routinely done with the help of the RS/1 data management system.

In the case of the Canada-Newfoundland Water Quality Monitoring Agreement, the analytical work is done in the water quality national lab, in Burlington, Ont. This lab uses the AWQUALABS data management system and has an intralab QA/QC program that is described in a document entitled "Quality Assurance in the National Water Quality Laboratory" (Agemian, 1986). Final validation of the data produced by the national lab under this monitoring program is done in Moncton. Both the Moncton regional lab and the national lab participate in a number of interlab QC studies every year. These studies are organized by the Quality Assurance and Analytical Methods Section of NWRI, and results are documented appropriately.

For many of the contaminants analyzed in various sample matrices within the toxic chemical survey project, there are no suitable standard reference materials (SRMs) available. Obviously,

this is a limitation on the accuracy of the results produced, and this limitation is presently unavoidable. Any report produced should indicate the origin of the calibration and working standards used for quantification, and also the reference materials used, when appropriate and applicable.

It is strongly suggested that the people dealing with toxic chemical survey activities (planning, field work, interpretation and report writing) should undergo some training in the lab by participating (assisting) in the extraction, clean-up and instrumental analyses steps, to get a "feeling" of the complexity of these kind of analyses. This involvement is needed for an appreciation of the difficulties met during the analytical work.

2. Field Trip Preparation

Prior to leaving for a field trip, it is the responsibility of the field technician to ensure that there has been adequate planning and that all necessary equipment has been packed and is in good working order. The present WQB field manual (1983, "Sampling for Water Quality") presents a detailed description of necessary preparation for every field trip and thus can be used as a reference check-list. An additional preparation that will be necessary for Atlantic Region personnel will be consultation with the project flowchart in order to determine which sites are to be sampled in sequential triplicate on a particular sampling trip.

3. Sampling and Field Analysis

3.1 Training of Personnel

In order to maintain consistent quality of data it is essential that all field technicians be thoroughly acquainted with all the WQB programs and the sampling and quality control procedures. This is particularly important for new personnel, who should be familiarized with project objectives, sampling protocol, station location and equipment operation prior to field work. In addition, it is suggested that new personnel read this document and the WQB field manual and be given an opportunity to discuss the material with staff members who are familiar with field operations prior to assuming any field duties. Present field staff should be required to review these two documents on an annual basis to ensure sampling protocols are being adhered to.

In the case where provincial staff are involved in water quality sampling (federal/provincial water quality monitoring agreement programs), proper training should be given by WQB personnel. This could be done in the form of a course on "water quality sampling" (Clair et al., 1986). Also, station microlocations and first sampling runs should be done in conjunction with WQB staff, to ensure compatibility between provincial and federal field procedures.

3.2 Sampling Procedures - General

As a result of the numerous WQB programs, several field technicians are usually involved in sample collection for each of the monitoring programs. Thus, in order to provide consistent, interpretable data, it is necessary to standardize general field sampling procedures.

Many WQB stations are located on bridges and thus provide ready access to any point across the waterbody. The main station is generally located at the mid-point and additional stations are established when spatial discontinuities are expected. All stations are located by permanent identification marks on the bridge structures. Although sampling from bridges has some obvious advantages, there are also some possible contamination problems. Most of these structures are constructed of metals, concrete or creosoted timber and thus caution must be exercised to avoid heavy metal, major ion and organic contamination, respectively. In addition, many of these structures are subject to heavy vehicular traffic and thus contamination by organics, heavy metals (i.e. leaded fuels) and road salts is a possibility.

In order to avoid this, all sampling should be conducted from the upstream side of the structure. When sampling from concrete structures care must be taken to ensure that the sample rope does not result in concrete dust formation by the abrasive action of raising and lowering the sampler.

Some of the WQB stations, require that samples be collected from the shore, which also results in QA/QC problems. Before establishing these stations it may be necessary to perform some cross-sectional sampling to ensure that the littoral samples are representative of overall water quality conditions. If samples are collected by wading, water should be taken upstream from the technician in order to avoid contamination by resuspended sediments.

Some samples are collected from stations which require the use of aluminum boats, rubber rafts and occasionally helicopters. Use of this equipment must be project specific with particular emphasis placed on the parameter list. Thus if heavy metals are the major concern the rubber boat should be used while the aluminum boat is more suitable for the toxic organic chemical program.

Regardless of the type of craft used, samples should never be taken off the stern of the boat, where floating oil and gasoline from the outboard motor might contaminate samples. For lakes which have poor accessibility, it is often necessary to use a helicopter, which due to fuel oils and kerosene fumes increases the possibility of toxic organic chemical sample contamination. Thus toxic organic water samples collected by helicopter sampling, must be viewed with extreme caution.

<u>In situ</u> measurements of selected water quality parameters (i.e. temperature, dissolved oxygen, pH and specific conductance)

form an integral part of the WQB sampling protocol. These measurements should be taken before actual water samples are collected in order to minimize water column disturbance caused by lowering and raising sampling apparatus.

This is particularly important for long residence time waterbodies and during periods of ice cover when the vertical distribution of many parameters may be highly variable. Once the in situ measurements have been completed water samples may be collected starting at the surface and proceeding down through the water column if applicable. Collection of sediment samples should be performed after all water column samples have been taken.

Water quality monitoring programs by their very nature necessitate sampling throughout the entire year, which can result in further QA/QC problems. This is particularly true of winter sampling where ice conditions and low temperatures have considerable influence on sampling protocol. Heavy ice conditions at many sites require the use of power ice augers and thus contamination of toxic organic chemical samples by gasolines and oils must be considered. In addition, during thaw periods there is often a layer of melt water immediately under the ice, which is not representative of the water chemistry of the system. Thus, care must be taken to ensure that samples are collected from a stratum well below the ice water interface.

Although in situ measurement of selected parameters is standard practice, winter results must be viewed with caution as many meters (i.e. pH meters) do not function well in cold temperatures. Conductivity meters such as the Hydrolab TC-2 may give erroneous results (usually biased low) if slush or ice is allowed to build up around the thermistor or in the conductivity cell.

Similarly, dissolved oxygen probes also can suffer from build up of ice and slush around the membrane. Thus, it may be necessary to determine winter dissolved oxygen concentration by the Winkler method, even though BOD bottle breakage and DO sampler freeze-up can also cause difficulties.

A final problem associated with winter sampling, involves sample handling. It is essential that water samples are not allowed to freeze prior to analysis. This is particularly important for samples with high concentrations of organic matter, as freezing and subsequent thawing can result in flocculation of dissolved and colloidal organic compounds. Thus, it is necessary to work from a heated vehicle, such as a mobile lab, during the winter months.

The WQB-AR is also involved in snowpack and precipitation sampling. However, very little of these activities are performed by WQB-AR field personnel, thus no description of procedures and equipment needed in these cases will be given in this report.

Interested readers are referred to the "Sampling for Water Quality" document (WQB, 1983) for description of precipitation sampling. A report of Sandberg et al. (1986) describes recommended methods for snowpack sampling and site selection.

3.3 Sampling Equipment

In the aquatic sciences, sample collection requires the use of a wide range of sampling equipment depending on the station, the medium to be sampled and the parameter list. Generally, the WQB-AR has used sampling irons or Kemmerer-Plus type sampling bottles for collection of water samples. The choice of sampler type must be closely related to the parameter list in order to avoid sample contamination. For instance, past experience with the PVC Kemmerer-Plus has indicated contamination of heavy metal samples. Where possible, sampler contamination will be tested by preparing demineralized water sampler blanks.

In addition to being parameter and station specific, samplers should be such that they provide suitable sample volumes and are suitable for use in a wide variety of environmental conditions. The sample volume is an important consideration as it is preferable that all sample bottles for an individual station be taken from the same sample. This is a measure which will assure that individual parameters are not being affected by short term temporal variation of the water mass.

3.4 Sample Bottles

Sample bottles are usually provided by the analytical laboratory. The bottles chosen must be free of contamination (including the liners and caps) and suitable for the parameter(s) to be analyzed. Table 1 list the recommended containers for specific parameter(s) and the washing procedures utilized to assure the cleanliness of the bottles. The volume of sample required depends on the type and number of parameters to be analyzed, the analytical method, and the expected concentrations of the parameters in the water.

Prior to sampling, every bottle should be rinsed twice with the water to be sampled. During the rinsing procedure, caps should be put on loosely to ensure adequate rinsing of the cap, liner and the bottle threads. If replicate samples are taken, every set of bottles should be rinsed twice and then filled, one set after the other (i.e. sequentially).

Proper identification of the sample is necessary to avoid possible confusion in the laboratory. All sample and sub-sample containers are affixed with a strip of vinyl labelling tape which, if applied to the containers when they are warm and dry, has been found to adhere well. Using a water-proof fine tipped Nylon marker, the NAQUADAT Station No., Sampling Date and Time, Parameter(s) to be analyzed and the program submitter identification (Sub. I.D.) is clearly printed on each container.

TABLE 1. Recommended containers and washing procedures for selected water quality parameters

Parameter(s) to be analyzed	Recommended container	Washing Procedure
Physical parameters Major Ions Nitrogen: NO_2-NO_3 Nitrogen: ammonia Nitrogen: total Dissolved organic carbon Dissolved inorganic carbon	1 L Polyethylene bottle	Rinse 3 times with tap water, once with chromic acid, 3 times with tap water, once with 1:1 nitric acid, and then 3 times with distilled water in that order
Suspended Solids	2 L Polyethylene bottle	Same as for physical parameters
Phosphorus, total	0.05 L Glass (Sovirel) bottle	Rinse 3 times with tap water, once with chromic acid, 3 times with tap water, once with 1:1 nitric acid and then three times with ultrapure distilled water, in that order
Metals, extractable	0.5 L Polyethylene bottle	Rinse 3 times with tap water, once with chromic acid, 3 times with tap water, once with 1:1 nitric acid and then 3 times with ultrapure distilled water, in that order
Chromium, extract.	0.25 L Polyethylene square bottle	Same as for metals but chromic acid is not used
Mercury	0.125 L glass (Sovirel) bottle	Rinse 3 times with tap water, once with chromic acid, 3 times with tap water, once with 1:1 nitric acid and then 3 times with ultrapure distilled water, in that order

TABLE 1. (CONT'D) Recommended containers and washing procedures for selected water quality parameters

Organic toxic chemicals	1 L or 4 L glass (amber) with Teflon-lined cap	Rinse 3 times with tap water, once with chromic acid, 3 times with organic free water, twice with washing acetone, once with pesticide grade acetone, twice with pesticide grade hexane and dry (uncapped) in a hot air oven at 360°C for at least 1 hour
Urea	1 L glass (Amber) bottle	Same as for organic toxic chemicals

Blank bottles should be similarly identified using a special NAQUADAT No. used to identify field blank samples.

3.5 Field Analysis: Field Meters and Calibration

At present, the Atlantic Region monitoring programs involve the routine measurement of four in situ parameters. These include water temperature, specific conductance, pH and dissolved oxygen. Prior to each field trip, all meters should be checked and laboratory calibrated. Fresh reagents for Winkler dissolved oxygen determinations should be prepared and the sodium thiosulphate solution should be standardized.

The precision thermistor temperature sensor of the Hydrolab Model TC-2 should be checked every 6 months against an ASTM certified Mercury Thermometer in the laboratory at temperatures of 2, 10, 15, 20 and 25^{o}C in a water bath.

The four-electrode configured specific conductance cell of the Hydrolab Model TC-2 should be checked before every field trip against the specific conductance of 2 freshly prepared standards at the 74 uS/cm and the 177 uS/cm levels. Instrument calibration is routinely checked at each sampling site by switching to the internal standards provided.

The combination glass electrode is calibrated daily in the field at pH values of 7.0 and 4.0 using commercially prepared pH

buffers kept at a temperature of $\pm$ 1.0°C from the sampling temperature. If the temperature of the pH buffers is not $\pm$ 1.0°C from that of the sample(s), it is adjusted by placing the buffer bottles in a colder or hotter water bath or in cold air (winter), whichever is applicable.

The YSI Dissolved Oxygen probe should be visually checked prior to a field trip, to verify the condition of the membrane. Defective membranes must be replaced. Everyday at the first site, D.O. concentration should be measured on two samples using the Azide modification of the Standard Iodometric Method (with freshly prepared reagents). These values are averaged and the meter is set (with the calibration knob) to read the average value of the samples. On the same day, only air calibrations are performed at the other sites. Calibration of the meter can also be accomplished using a calibration chamber, in which the D.O. probe is placed, and then immersing the chamber in the stream or lake to carry out the measurement, at a given site. The latter approach provides an adequate environment for proper calibration.

3.6 Field Analysis: General

Field personnel should keep a record of observations on meter operation and any malfunction or suspected problems should be noted. This may help data interpreters to explain spurious data, during the data interpretation process.

Historical site summary data (minimum, maximum, median) and/or graphics (parameter over time) should be provided to non-WQB collectors to permit them to evaluate how their in situ measurements from a particular site compare with those historical data originating from that site. Where applicable (WQB routine sampling projects), it would be useful to have cumulative frequency curves for specific conductance (historical data for each site). This could be helpful in identifying a special event, spill, etc., requiring additional sampling effort.

The proposed standard procedure for in situ specific conductance measurement is that the probe be removed and re-submersed in the water body three times to check for repeatability of the measurement. This will offset the great majority of errors in the field specific conductance readings that are caused by either slush and ice chip interfering with the geometry of the cell in the winter, or sediment, etc., in the summer months.

Suitable air thermometers should be provided for all field vehicles to permit ambient air temperature measurement at each site.

A routine procedure to check on the field measurement (generally pH and specific conductance) performance of non-WQB field staff could be as follows. The WQB-AR would prepare special QC samples, consisting of buffer solutions and natural waters (in

an appropriate range of ionic strengths). These would first be analyzed in the lab and their stability verified. These QC samples would then be sent out to non-WQB field staff for analyses. These samples along with the non-WQB field staff results obtained would then be returned to the WQB-AR lab for compilation of results and re-analysis of the samples. Performance reports would be prepared and sent back to the collectors as part of a feedback process, thus the non-WQB personnel would have a means of knowing how well they are performing. However, implementation of this evaluation procedure could cause some logistical problems.

3.7 Field Record Keeping

Casual observation, relevant meteorological data, field measurement data, sampling and testing problems, and corresponding dates and station number should be recorded in the field notebook. Field technicians should be aware that unusual conditions may necessitate some in situ modification to the normal sampling protocol. These modifications may provide meaningful auxiliary data provided that they are properly documented.

The interpretation of water quality data cannot be accomplished without all the supporting information. Observations of weather, fish kills, abundant algal growth, slicks on the water surface and other phenomena may make a significant difference in explaining anomalies in data. Therefore, all observations should be recorded, no matter how trivial they may seem.

At the end of either the day or the field trip, the field record sheets should be completed using the data and information recorded in the field notebook. These field sheets will then be delivered to the laboratory along with the samples. Also, the field project book should be completed (updated) at the end of the field trip. This book should contain all data, observations and problems recorded in the field notebook for each field trip. This field project book will be accessible for those persons scrutinizing the analytical results when they are released from the lab.

3.8 Sequential Triplicate Sampling

Commencing on April 1, 1984, as a mean of controlling and assessing the quality of our water chemistry data, approximately 15% of all samples have been collected in sequential triplicate. This procedure is implemented on a project basis and includes samples for the entire suite of parameters generally measured in each individual project.

For those projects which have a small number of stations, one triplicate sample is collected for each sampling trip and thus in practice, replication may reach 20-25% of all samples collected. For those projects which use non-WQB collectors, triplicates are taken for at least 20% of all samples collected. The experimental design of this triplicate sampling procedure is such that results

can easily be analyzed by region, project, station, technicians and season, and thus may serve to elucidate serious quality difficulties.

In order to ensure equal weighting within projects, stations to be replicated are selected from a predetermined rotational schedule. This overcomes the possibility of field technician bias towards easily accessible stations. Triplicates are collected on a sequential basis after all bottles have been properly rinsed with sample water. It is important to do one sample (group of bottles) at a time, one after the other (sequentially). It generally takes less than 15 minutes to collect a sequential triplicate sample.

The sequential triplicate sampling program serves to evaluate whether the water sampling performed is representative. Also, in the case of inadequately replicated parameters, it aids to discern contamination and/or analytical problems. In some cases, it is possible that the grab sampling of unmixed river water is causing the disproportion between a set of triplicates, and field observations become a very important tool to ascertain these triplicate results. In addition, the triplicate results reveal problems associated with water quality data management. Overall, the sequential triplicate sampling covers the entire quality assurance picture by providing some information on the combination of field, laboratory, and data management components.

If a problem is revealed by this sequential triplicate sampling, it does not mean that the source of this problem will be determined exactly, but other quality control measures (field and/or laboratory) may then be required to elucidate it. It is probably correct to look at the sequential triplicate sampling as an indicator of the performance of the whole monitoring work instead of as a tool that will precisely define the exact source(s) of a problem. It indicates problems and will also aid in determining the causes of these problems.

Other QA/QC measures do exist to monitor the performance of field work. One example is the preparation of field blanks. This aspect will be treated later in this text.

Triplicate rather than duplicate sampling was chosen in this field QA/QC program, because it was felt that adding a third sample would be helpful to determine the nature of the problem. In fact, it was observed (Arseneault and Howell, 1985) that in many cases where a problem occurred, the occurrence was in only one of the three samples within the triplicate. It was felt that sampling more than three times (quadruplicates or more) would have put the overall cost of the QA/QC program much higher without getting much more information from it. However, this procedure of sampling sequential quadruplicates (or more) may be used in response to a specific problem regularly observed with a given parameter of interest. In addition, splitting of samples may be required to

investigate other types of problems revealed by the present sequential triplicate sampling program.

The WQB-AR field QA/QC program will evolve with time, but first there is a need to create a consistent QA/QC data base from which to design the future steps of this field QA/QC program, in response to the problems that have been observed. As previously mentioned, the sequential triplicate data base, which is presently comprised of more than 500 triplicates, is being assessed. Frequency of triplication should remain the same (15-20% of all samples) until this data assessment is completed and recommendations made.

3.9 Sample Preservation and Filtration

All necessary preservatives are prepared in the laboratory by ASD personnel using ACS or Ultrex grade chemicals. The field repipet dispensers are washed after each sampling trip and refilled with appropriate volumes of new preservatives.

At present the WQB-AR routinely preserves metals, phosphorus and mercury samples (Table 2) as well as the occasional preservation of selected toxic organic chemical sample (see section 4.1). As preservation is often performed in the back of open vehicles, it is felt that random site specific sample contamination is minimized by preserving the samples at the end of the day.

In addition to sample preservation, field blanks are prepared at the end of each day for each of the preservatives used. This is achieved by adding the appropriate preservatives to sample bottles containing deionized distilled water. In the past, large carboys of ultra-pure distilled water for use as rinse water and for blank preparation were taken on each trip. However, as this water had remained in these containers for varying lengths of time, it was felt that contamination by leaching of materials (i.e. metals) from the vessel walls was a possibility. Therefore, commencing April 1, 1984, the regular sample bottles are filled with ultra-pure distilled water prior to departure for the field. These bottles will then be preserved where appropriate and used as field blanks.

TABLE 2: Procedures employed for preservation of water quality samples collected for inorganic parameter analyses

Parameter	Preservative
Metals	1 mL Conc. HNO_3/500 mL sample
Phosphorus	0.5 mL 30% H_2SO_4/50 mL sample
Mercury	1 mL Conc. H_2SO_4, 1 mL 50% $K_2Cr_2O_7$ solution/100 mL sample

In the case of non-WQB collectors, it is necessary to make certain adjustments to the sample preservation protocol. In the WQB Regional Overview Network, WRB hydrometric technicians collect and preserve water samples from selected rivers. Initially, the WRB personnel were supplied with preservative dispensers; but these were too fragile for rugged field application. Therefore, the dispensers were replaced by vials which held individual portions of preservatives. However, this procedure affords no quality control and contamination of both blanks and samples has been observed. As a result of this, all samples collected by WRB hydrometric technicians, since April 1984, are not preserved until the samples reach the WQB-AR laboratory in Moncton. Appropriate preservative blanks are then also prepared.

The same approach presently applies for samples collected by the Newfoundland government regional field officers, but in this case samples are analyzed in the national lab in Burlington, Ontario. This lab preserves the samples upon receipt and prepares appropriate blanks. It is not known with certainty if this procedure of preserving samples days after collection will significantly change the results obtained. However, all parameters concerned by this procedure are extractable or total parameters, and thus no problem is expected. Work done by Miller et al. (1985) tends to support our thoughts on this subject.

To determine the concentration of dissolved inorganic constituents, it is necessary to pass the sample through a filter

of specified porosity, type and quality. The filtrate should be preserved (if required) by adding the proper preservative. The glassware utilized should be specific to the parameter to be analyzed and thus filtrations of samples for dissolved phosphorus and samples for dissolved aluminum would require two sets of glassware and tubing. The filtering apparatus should be placed in transportation cases that permit proper storage and provide protection against shock and dirt. These cases should also provide stable work platforms for filtration.

Presently, in the Atlantic Region, field filtering is done for dissolved phosphorus and dissolved aluminum. For dissolved phosphorus, Gelman Spectrograde Glass Fiber filter, 47 mm diameter (99.9% efficiency for removal of particles of 0.3 um) are used. For dissolved aluminum, Millipore membrane filters, 0.45 um (white plain surface) are used. Filters and apparatus are washed with 5% HCl solution for phosphorus and 5% HNO_3 solution for aluminum. Then, they are rinsed with ultra-pure distilled water and used.

All glassware is rinsed with ultra-pure distilled water prior to filtration and between filtration of individual samples. The glassware and filter are rinsed by filtering the excess water, and the sample bottle is rinsed twice with filtrate.

Filtrations are performed at the end of the day, to ensure the same conditions for all samples. A filtration blank for each parameter are prepared from ultra-pure distilled water using the

same procedure as for a sample. At the end of a filtration set, the glassware is rinsed with diluted acid solution and afterwards with ultra-pure distilled water. The handling of filters and glassware is kept to a minimum in order to avoid possible contamination.

In the past, the WQB-AR employed plastic crates as a means of carrying sampling bottles in field vehicles. Although these crates provided a convenient method of bottle and sample orgnization, they failed to remove samples from direct sunlight and were unable to regulate temperature. In order to keep samples dark, all bottles are now carried in coolers. This serves to overcome chemical transformaton due to photo-oxidative processes and/or biologically mediated reactions.

A general practice for maintenance of the quality of both preserved and unpreserved water samples is refrigeration at $4^{o}C$. At present this procedure is not employed for WQB samples until they are received back at the Moncton laboratory. For some programs, this may represent a four or five day period.

In the future, attempts will be made to refrigerate samples while in the field with priority given to unpreserved samples. The WQB-AR Mobile laboratory is equipped with a refrigerator, so that sample refrigeration in the field presents little difficulty. However, in the other field vehicles, it will be necessary to use "Koolatrons" to keep samples refrigerated.

In order to ensure continual refrigeration of water quality samples, it will be the field technicians' responsibility to plan field activities such that expedient return of samples to the laboratory is possible. If arrival back at the Moncton laboratory is expected after working hours, prior arrangements must be made to provide temporary refrigerated storage, until the samples can be processed through the system.

4. Sampling for Toxic Chemicals

This section, as previously mentioned, was not completely covered in an earlier draft report prepared in 1984. All the field procedures described herein are generally specific to the toxic chemical work done by the WQB-AR. All appropriate procedures mentioned earlier in this document are still applicable, but it was felt that this type of work required more field and lab QA/QC effort than other activities, because of its more complex nature.

This section will deal mainly with the trace toxic organic chemical sampling protocols although the same applies for trace toxic inorganic chemical (metals) parameter determinations. However, in this case, the analytical, sampling and preservation processes involved are somewhat less complex and thus require fewer QA/QC procedures.

In the toxic chemical survey projects, water, bottom sediments, fish (forage and predator) and other biota samples are collected. Sampling and specific field QA/QC procedures in use for each medium will be described here. In addition, a number of recommendations to upgrade our QA/QC program in this particular area are made throughout the text. Section 5 summarizes these recommendations and others made earlier.

Note that, under certain field conditions, as for example, work in Labrador or in other remote areas, some field QA/QC procedures listed later in this text could be difficult to follow without modification. Thus, some changes to the protocols may be warranted in such cases.

On the laboratory and interpretation sides of toxic chemical activities, there are some areas that are often overlooked or underestimated, but which require much more work and understanding. These are the significance of limits of detection, the differentiation of analyte from background and the confirmation of trace organics by other analytical techniques. However, discussion in these areas is beyond the scope of the present document.

4.1 Water

Water samples for toxic organic chemical analyses are collected in the same manner as any other water sample. Generally, 4 L amber glass bottles with Teflon-lined caps are used. Rinsing

of these bottles in the field is not required. A list of some water sample preservation procedures followed in the field, for toxic chemical work, is given in Table 3.

Starting fiscal year 86/87, the WQB-AR has instituted in its toxic chemical survey projects, improved field QA/QC procedures, with regards to water sampling. These procedures are as follows:

- preparation of field blanks;
- preparation of spiked field blanks;
- preparation of spiked field samples (often in replicates);
- sequential replicate sampling;
- preservation of spiked blanks and samples a few hours after spiking, to permit interaction between sample matrix and spiking solution.

Previously, the WQB-AR field staff generally prepared only spiked field samples (often in replicates) with immediate preservation. This provided the Branch with some interesting data. However, irreproducibility of replicate spikes were observed, and this led to the conjecture that there was a time dependent interaction between the spike and the matrix. This new scheme is designed to address this question.

TABLE 3: Procedures employed for preservation of water samples collected for toxic chemical analyses

Parameter	Preservation
Organochlorine pesticides Organophosphorus pesticides Polyaromatic hydrocarbons Polychlorinated biphenyls	Add 200 mL of hexane per 4 L sample (in a 4.5 L amber glass bottle), shake well and deliver to the lab as soon as possible. Place a piece of aluminum foil over the mouth of the bottle before screwing on the cover (except when there are teflon liners in caps).
Chlorophenols	Adjust to pH 4 with 25% H_2SO_4.
Carbamates	Adjust to pH 3 with 25% H_2SO_4.
Chlorobenzenes	Add 50 mL of hexane per 1L sample and shake.
Triazines	Adjust to pH 8 with 0.1 N NaOH solution, add 200 mL of methylene chloride per 4.5 L sample and shake.

NOTE: - All samples are kept as cool as possible in the field.

A field blank is prepared by adding "approved" distilled or natural water to a sample bottle prior to a field trip. The preservatives are then added in the field when samples are also preserved, which is then called a field blank. This is done to check on the cleanliness of sample containers, random field contamination and the purity of added preservatives. In addition, the analytical lab also runs solvent blanks when they do the

analyses.

Prior to its use in blank preparation, the water (distilled or natural) should be checked through its analysis in the lab. It is possible that it may require some treatment (solvent extraction, filtering through XAD type resin columns, ...) before it is approved. In the summer of 1986, the WQB-AR decided to use filtered Turtle Creek water (Moncton's drinking water supply) in the preparation of field blanks because the distilled water showed some contamination which interfered with the analytes of interest.

Preparation of spiked field blanks is also required to check on the recovery of a spiked analyte of interest in a "clean" matrix. All spiking solutions are prepared by lab personnel prior to field trips. Preparation of spiked field blanks also serves to verify on the behavior (stability) of the spiking solution in a "clean" matrix and the accuracy of its preparation. These spiked field blanks are prepared at the same time that spiked field samples are prepared in the field. Analytical results of the two are then compared to see if the analytical process is recovering analyte as well in a natural sample (matrix effects) as in a blank (no matrix effects). The resultant data can then be used appropriately during the data interpretation process.

Spikes are prepared by using an appropriate micro-syringe (previously solvent rinsed) to add a precise volume (generally 100 or 200 uL) of a spiking solution (of known concentration) into

blanks and/or regular samples. All field personnel involved in the preparation of spikes should first be trained to use a micro-syringe. It has been suggested that larger volumes of less concentrated spiking solutions may be appropriate for the preparation of spikes. This would minimize possible manipulation errors when adding a spiking solution to a sample.

Spiked samples are generally prepared in replicate (duplicate or triplicate) in the field, to verify the reproducibility of spike recoveries and to gain a better understanding of the spiking process. It is recommended that replication of spikes should be done on all occasions. Based on resource availability, duplication of spikes would be an acceptable minimum, although triplication would possibly give more information. The preservation of spiked blanks and samples is now to be effected a few hours after spiking, and this should permit an interaction between the sample matrix and the spiking solution, before it is extracted.

In terms of reporting the analytical results on these spikes, both the absolute concentrations and the percent recoveries will be reported by the lab on the computer. Presently, only the absolute concentrations are reported, which is not very useful when looking at historical spiked sample data, as there is no record of the concentrations of spiking solutions used. Thus, some provisions for storing the percent recovery values on the computer will be made for all spiked samples and blanks.

The frequency at which this set of field QA/QC samples (blank, spiked blanks, spiked samples (in replicate)) should be prepared is dictated by the study itself. However, a minimum would be a complete set of these field QA/QC samples at least once per week per basin surveyed. This is in anticipation that the general water characteristics (colour, turbidity, pH and specific conductance), on any given surveyed basin, are fairly stable during that week.

If conditions change during the week, as, for example, the occurrence of a heavy rain-fall with resulting high runoff period and suspended solids load, then one additional set of the field QA/QC samples should also be prepared. This will be done to account for the differences in matrix of water samples collected under various conditions, in any given basin under study. If samples are collected from many basins and the general water characteristics are very different between these basins, then one set of field QA/QC samples will be prepared per basin.

Sequential replicate sampling should also be regularly done in addition to the above activities, in a random fashion. It is recommended that sequential triplicate sampling be done at least for 10-15% of all samples collected. This is a way to check on the short term temporal variability of the parameters under study, in the matrices sampled. In addition, it may permit the discernment of contamination problems and/or sources, when considered together with results obtained from other field QA/QC samples described earlier. It is strongly recommended that lab spiked samples should

be prepared and analyzed routinely in order to compare results with those attained by field spiked samples. For this purpose, extra samples should be collected.

In 1986, the WQB-AR began to use, what is called a "Crab APLE Extractor" (Fox, 1985), which permits the extraction (liquid-liquid) of 40 L of water directly in the field. The 40 L sample is previously filtered by this device and the suspended solids retained on the filter can also be kept for analyses. This extractor permits detection of very low concentrations (sub-ppt) of organic contaminants. However, the purity of the solvent used is extremely important, as large quantities of solvent are needed to extract the 40 L sample.

This type of extractor is relatively inexpensive and readily available. Water collection, filtration and extraction of both phases can be accomplished in the field in less than an hour. Fox (1985) presented some data on recoveries of organochlorine spiked organic free water and natural Lake Ontario water. In general, recoveries were very good. However, this was limited only to organochlorine contaminants, and thorough testing of this extractor is being conducted for other contaminants of interest.

This type of extractor is very useful in specific type intensive surveys where, for example, a pond is sprayed with a pesticide and the survey is aimed at studying the behavior of this pesticide in water (and suspended sediments) over time. In the

case of toxic chemical screening or in any surveillance project, the usual sampling of 4 L water samples is adequate, since sufficiently low detection limits ($\leq$ 0.01 ppb) are already attained for many organic contaminants with this sample volume. In addition, most water quality criteria, guidelines or objectives set for toxic organic chemicals are generally higher than this 0.01 ppb.

Regardless of this, the "Crab APLE Extractor" should be thoroughly assessed in terms of QA/QC aspects, and consistent protocols developed for its use in those specific studies requiring this type of extraction system and detection limits. These protocols should include preparation of field blanks and field spikes, to verify the recoveries attained by the extraction and any possible contamination originating from the use of this extractor.

One very positive aspect with this type of extraction system, is its capacity for filtering the water and retaining the suspended solids on a filter for analyses. It could be used routinely for this purpose only. Another interest of a wider utilization of this type of extraction system would be for loading calculation purposes. However, one could question the validity of this application, in light of the lower confidence level attained by the sub-ppt contaminant concentrations measured in water. In other words, to be able to detect very low concentrations, this extraction system introduces more variables in the sampling and analytical processes. The accuracy and precision of the

identification and the quantification will suffer from this extra burden in an already very complex situation.

In the past, the WQB-AR has made use of Amberlite XAD-4 resin columns in the field for sampling (extraction) of fenitrothion and aminocarb in rain water (O'Neill and Bailey, in prep.). The rain water was collected and extracted with the aid of a special sampling (collection) device equipped with Amberlite XAD-4 columns. The sample columns were replaced every week by fresh ones. The sample columns were brought to the lab, and eluted, with an appropriate solvent, for the parameters of interest. These parameters were then identified and quantified analytically. After elution, the columns were regenerated with specific solvents, wrapped in clean aluminum foil and returned to the field. It is felt that these types of extraction columns could have other applications in the field, one of which could be extracting large volumes of surface water for the determination of specific organic contaminants (Woodrow et al., 1986; Leenheer and Noyes, 1984). However, one problem with resins is that they require exhaustive cleaning with various solvents to remove all trace contaminants.

If these Amberlite XAD-4 resin columns (or others) are used more extensively in the future, consistent sampling and QA/QC protocols could be developed. In terms of the specific field QA/QC procedures that are needed, preparation of blanks, spiked blanks, spiked samples (in replicate) and sequential replicate sampling should be included to routinely check on the purity of the resin

column, the cleanliness of the apparatus, the recoveries attained by the extraction and elution processes, the reproducibility of the extraction and elution efficiencies and the representativeness of the water samples.

4.2 Bottom Sediments

Bottom sediment samples are collected with a 15 x 15 cm or 30 x 30 cm Ekman grab sampler and transferred to a pyrex tray. Toxic organic chemical samples are taken from the top 2.0 cm of sediments with an aluminum scoop. A similar sample is taken for heavy metal determinations with a plastic scoop from the centre of the grab sample in order to avoid sediments which have been in direct contact with the dredge.

Three or four (or more) grabs are taken and the top 2.0 cm of sediments of each grab are put in a large plastic or stainless steel bowl (depending on the type of analyses required). Then, the bottom sediments samples placed in the bowl are mixed together, using an appropriate scoop to get a well homogenized sample. Subsamples (often triplicate splits) are then delivered to individual aluminum containers or, in the case of samples to be analyzed for metals, to Whirl Pak polyethylene bags and frozen until analysis.

It is recommended that these aluminum trays be replaced by another type of container which will better maintain the integrity

of the samples on freezer storage, for example, glass jars. All apparatus and containers involved in the collection and storage of sediment samples for organics are prewashed and rinsed with acetone and hexane.

The previous paragraphs have outlined the approach presently being used by the WQB-AR for sampling bottom sediments. However, it is felt that additional study is required to improve the representativeness of the bottom sediment samples. Perhaps the top 2 cm of sediment is not the proper fraction to sample. In addition, Ekman grab samplers may be inappropriate for this type of work. Some research in this area should be done and documented.

In addition to determining the concentrations of the selected parameters, each bottom sediment sample is characterized by measuring water content and percent organic carbon (CHN analysis). This information is essential for interpretation of toxic chemical analysis results. In some studies, samples are also characterized through particle size analyses.

Care must be taken when sampling bottom sediments to preferably get samples with high clay and organic matter content instead of rocks and sand, because it is known that pollutants are likely to be observed in the former type of bottom sediment matrices. Obviously, this is placing a bias on the sampling site selection, but adherence to this criterion must be encouraged. Generally, bottom sediment samples are taken from an enlargement of

a river, which permits deposition of suspended sediments on the bottom. In a lake, the situation is usually less critical. Samples are usually collected from the deepest point of a lake (when "screening" is the study objective). However, in the last three years, we have tried to get a better coverage of the spatial variability of the quality of bottom sediments, by sampling many sites within any given surveyed lake or river.

Similar to what is done in water, spiking of bottom sediment subsamples, with organic contaminant standard solutions, is done regularly in the field. The procedure employed is to weigh about 20. g. of bottom sediments in a sample container (generally aluminum and pre-washed). Then 100 or 200 uL of spiking solution is added and mixed with the sample. Following this, the container is closed and stored in a freezer.

It is felt that this spiking procedure has many defects. One problem arises from the fact that the containers presently used are much too large for containing only 20. g. of spiked samples. For regular samples, these containers are generally completely filled. It is suspected that such a container filled with only 20. g. of sample is not airtight, and that volatilization of some of the spiked contaminants may occur. Thus, the containers used to keep spiked samples should be replaced.

In late 1986, the WQB-AR had switched to using 50 mL Sovirel bottles (pre-washed) for preparation of spiked bottom sediment

samples. For the moment, it is suggested to continue their use as they are better suited for this purpose than the aluminum containers used for regular samples. However, this adds another variable to the sampling procedure. If a new type of container is chosen for regular samples, then the same one should be used for spiked samples. Perhaps a parameter specific container could be used in the future. This option will be considered.

Another problem is that there are presently no "reference" samples of bottom sediments that can be used to prepare field blanks and spiked field blanks. However, it is proposed that a bank of "reference" bottom sediments be prepared for this purpose. As is the case for water, blank and spiked blanks are needed to check on contamination caused by containers, and on accuracy, reproducibility, stability and recovery efficiency of the spiking process. To do this with sediments, we need some sort of "reference" bottom sediment bank, which will furnish the material needed.

This "reference" bottom sediment bank would consist of a large bottom sediment sample, which would be previously approved by the lab through subsample analyses and spiked subsample analyses and recoveries. It would also have to be sterilized and kept this way in order to eliminate any biological activity that could have an effect on the integrity of spiking solutions added, when preparing field spiked blanks. For storing and handling purposes, it may be better to dry it, and rehumidify portions of it, as needed.

With the use of the standard reference material, it would then be possible to compare spiked bottom sediment sample recoveries against spiked bottom sediment blank sample recoveries, which was previously a missing link when trying to understand the resulting data. It may be that such a bottom sediment SRM is already available (NWRI, EPA, ...), if so, the WQB-AR will endeavour to acquire this material.

Some QA/QC testing of the storing procedure presently used for bottom sediments is recommended. As previously mentioned, bottom sediment samples are frozen after collection, then brought to the lab where they are kept frozen until analysis. Samples are then thawed by a lab technician, so that an aliquot can be obtained for certain parameter analyses; after aliquot extraction(s) the samples are refrozen. Before taking an aliquot, samples are homogenized as best as possible in the container, (with some difficulty in aluminum containers). Another aliquot is taken for analyses of other parameters within a few days (or weeks), and the same bottom sediment sample will be thawed and refrozen. This procedure will be repeated until all analyses and rechecks are completed.

The effect this multiple thawing and freezing has on the contaminants of interest present in a sample is unknown. Also, when thawing a bottom sediment sample, a water layer is very often observed in the container, the extent of this depends on the type of bottom sediments collected. What happens to this water? Are

the chemicals of interest present in this water (released by the sediment particles with water during thawing)? Is it well homogenized with the rest of the sample? Should we also analyze this water? Lab analysts have indicated that it is very difficult to properly homogenize thawed bottom sediment samples in the aluminum containers presently in use.

Another questionable area has to do with the stability of the complex formulations of spiking solutions (this is also applicable for water, as the same spiking solutions are used). Are there interactions of some sort (chemical or physical) between the various chemicals in a spiking solution, and could this have an impact on the solution's integrity? However, preparation of spiked bottom sediment blanks would certainly help in controlling the integrity of spiking solutions used, over time.

As presented here, many areas in our toxic chemical work are fraught with uncertainty. It is strongly suggested that some of these gaps be filled soon. This could be done in the form of special QA/QC studies designed specifically to answer these questions. It could also be presented as research proposals to NWRI. Other problem areas not mentioned here do exist and should also be looked at in the future.

In terms of frequency of preparation of bottom sediment blanks, spiked blanks and spiked samples, an approach similar to the one followed for water sampling should be taken. This

essentially consists in preparing at least one set of these field QA/QC samples per week, with extra ones required when working in highly variable conditions. Preparation of lab spiked bottom sediment samples, on a routine basis, is also strongly suggested. This would permit comparisons between results of spiked samples prepared in the field and in the lab.

4.3 Biota

With respect to quality assurance, the collection and interpretation of biological data is more difficult than for water or bottom sediments. Many of the organisms collected are mobile and thus it is difficult to class them as representative of the site from which they were taken.

The present biological sampling activities of the WQB-AR is centred on collection of fish, with occasional sampling of freshwater clams, macrophytes, phytoplankton and zooplankton. Fish are collected by gill and seine netting, depending on the species required. For toxic organic and inorganic chemical analyses, small size fish species are pooled in order to provide adequate sample volumes while large fish are dissected, and the egg mass, livers and muscle are analyzed separately. Care must be taken during dissection to avoid cross-contamination of samples. Samples are stored in aluminum containers or aluminum foil (for toxic organic chemicals analyses) or plastic bags (for metals analyses) and frozen until analysis.

The major quality assurance procedure presently in place is to maintain statistically significant sample sizes for each site, although our experience with fish sample collection was not always very successful in the past. In addition, where appropriate, age, size, weight and lipid content will be determined to aid in data interpretation. Dissection of fish by WQB-AR personnel is generally done directly at the site of collection. All dissecting equipment and sample containers are prewashed appropriately.

Freshwater clams are collected either by hand in the shallow littoral zone or by a benthic drag in deeper regions. The clams are shucked and pooled to provide adequate sample volumes, and then stored in a manner similar to the storage of fish tissue. In addition to determination of toxic organic and/or inorganic chemicals concentrations, species identification, sex, shell length, total weight and body weights are determined for each organism. As was the case for fish, the additional informaton is useful for data interpretation.

In addition to fish and freshwater clams, other biota such as macrophytes, phytoplankton and zooplankton are occasionally sampled. However as they are sampled infrequently, no standardized procedures have been established other than to treat them in a similar fashion to fish and freshwater clams.

No field spiking of biota has been attempted by the WQB-AR. To do this, a sample processor (grinder, homogeniser) of some type would be needed in the field to prepare and mix samples with spiking solutions. The extra manipulations required in this case would probably lead to more field contamination problems. However, it is recommended that the lab regularly prepare such spiked samples, to verify (performance evaluation) on the efficiency of the analytical process involved here.

It does not mean that a good spike recovery would indicate a good environmental contaminant recovery from any given sample, but if the spike recovery is not so good, then it is very possible that the analytical process used is not able to accurately determine concentrations of contaminants "environmentally" present in a sample. This is the type of routine control required to ascertain some degree of quality in our work with biota. However, it is important to mention that most of the parameters analyzed in biota are heavy metals. Organochlorine pesticides and PCB's are the only organic contaminants presently routinely analyzed in biota by the WQB-AR.

It is worth mentioning here that the WQB-AR has developed its own biological data management computerized system (Howell et al., 1985). This had to be done because there has been more emphasis put on biological work in recent years and because the NAQUADAT system does not permit proper storage of biological data. To have

adequate data storage and retrieval capacities is part of a good overall QA/QC program.

5. Recommendations

This section summarizes all recommendations made throughout the report. First, general recommendations are presented. These are followed by recommendations specific to toxic chemical work.

General

1 - Field QA/QC procedures as outlined in this document should be followed in all WQB-AR projects.

2 - All QA/QC results produced should go on the computer. Proper coding is needed for easy retrieval.

3 - New personnel should be given the opportunity to read this document and other pertinent WQB documents on field work and related QA/QC activities, and discuss these with staff familiar with field operation, prior to assuming any field duties.

4 - People dealing with toxic chemical survey activities should undergo some lab training in this field to get a "feeling" of the complexity of these kind of analyses.

5 - Sequential triplicate sampling frequency should remain at 15-20% until the sequential triplicate data base assessment is completed. Recommendations will then be made concerning the triplication program.

6 - The laboratory should not spend more effort on triplicate samples than that spent for any other regular sample submitted for analyses.

7 - The project leader should be advised as soon as possible of any changes in lab methodologies for parameters of interest in his project(s).

8 - When another agency is involved in water quality sampling for the WQB-AR, station microlocations and first sampling runs should be done in conjunction with WQB staff, to ensure compatibility in field procedures.

Toxic Chemical Work

Water

1 - All QA/QC procedures implemented during fiscal year 1986/1987 should be continued.

2 - Proper training on micro-syringe operation should be given to all field personnel involved with field spike preparation. Larger volumes of less concentrated spiking solutions could be used in future field spike preparation.

3 - Sequential triplicate sampling should be done for 10-15% of all samples.

4 - One set of field QA/QC samples should be prepared per week, with extra ones required when general water characteristic conditions vary during the same week (during a survey).

5 - Duplicate spikes should be prepared on all occasions.

6 - Routine preparation and analysis of lab spiked samples is strongly recommended. This would permit comparisons between lab and field spiked sample recoveries.

7 - The "Crab APLE Extractor" could routinely be used only for collection of suspended solids, for analyses of selected toxic chemicals. Its use for water sampling should be limited to specific studies.

8 - More QA/QC testing of the "Crab APLE Extractor" is needed before expanding its use.

Bottom Sediments

1 - Aluminum trays presently used for bottom sediment samples should be replaced by a better type of container. This change in container is proposed to better maintain the integrity of samples and spikes on freezer storage.

2 - A reference bottom sediment bank is required to prepare spiked bottom sediment samples. If such a Standard Reference Material is available on the market, the WQB-AR should acquire some. If not, a request could be addressed to NWRI, or the WQB-AR may have to prepare its own.

3 - Some QA/QC testing of the storing procedure presently in use for bottom sediment samples is recommended to:

- verify the effects on contaminants of interest of multiple freezing and thawing endured by samples during the whole analysis period;

- verify contaminant concentrations in the water released by thawed bottom sediment samples;

- propose solutions if these are proved to be problems.

4 - In terms of frequency of preparation of bottom sediment field QA/QC samples, the same approach as for water should be taken.

5 - Routine preparation and analysis of lab spiked bottom sediment samples is strongly recommended. This would permit comparisons between lab and field spiked sample recoveries.

6 - Some work on bottom sediment sample representativeness should be done, as this aspect was never thoroughly studied by WQB-AR.

Biota

1 - Routine preparation and analysis of lab spiked biota samples is strongly recommended.

References

ACS Committee on Environmental Improvement, 1980. Anal. Chem., 52:2242.

ACS Committee on Environmental Improvement, 1983. Anal. Chem., 55:2210.

Agemian, H. (Coordinator), 1986. Quality Assurance in the National Water Quality Laboratory. 2nd Edition, Inland Waters Directorate, Environment Canada, Burlington, Ont.

Arseneault, R., G. Howell, and D. Lockerbie, 1984. The Water Quality Branch Atlantic Region Field Quality Control/Quality Assurance Program. Draft Report, Water Quality Branch, Environment Canada, Moncton, N.B.

Arseneault, R., and G. Howell, 1985. Field Quality Control/Quality Assurance Program. Results of 1984/1985 Sequential Triplicate Sampling. Tech. Rep. IWD-AR-WQB-85-78, Water Quality Branch, Environment Canada, Moncton, N.B.

Bailey, H.S., 1984. Survey of Toxic Constituents in the Atlantic Region's Aquatic Environment - 1982. Tech. Rep. IWD-AR-WQB-84-55. Water Quality Branch, Environment Canada, Moncton, N.B.

Bailey, H.S., 1985. 1983 Toxic Chemical Survey of Nine Impoundments in the Saint John River Basin. Tech. Rep. IWD-AR-WQB-85-88, Water Quality Branch, Environment Canada, Moncton, N.B.

Blaise, C., N. Bermingham and R. VanCoillie, 1985. The Integrated Ecotoxicological Approach to Assessment of Ecotoxicity. Water Quality Bulletin, Vol. 10, No. 1, Environment Canada, Burlington, Ont.

Brun, G.L., 1986. Quality Control Activities During 1985. Atlantic Region Water Quality Laboratory, Water Quality Branch, Environment Canada, Moncton, N.B.

Chau, A.S.Y. and J. Lawrence, 1984. Quality Assurance of Environmental Measurement: An Overview. National Water Research Institute, Environment Canada, Burlington, Ont.

Clair, T.A., D.M. Lockerbie, H.S. Bailey, R.A. Arseneault, R.A. Bingham, G.L. Brun, 1986. A Basic Course in Water Quality Sampling. First Edition, Tech. Rep. IWD-AR-WQB-86-106, Water Quality Branch, Environment Canada, Moncton, N.B.

Clair, T.A., H.J. O'Neill and H.S. Bailey, 1987. Pesticide Survey of the Dunk River and South West Brook Basins - Prince Edward Island, 1985. Tech. Rep. IWD-AR-WQB-87-117, Water Quality Branch, Environment Canada, Moncton, N.B.

Fox, M.E., 1985. A Practical Sampling and Extraction System for the Quantitative Analysis of Sub ng/L of Organochlorine Contaminants in Filtered Water and Suspended Solids. National Water Research Institute, Canada Center for Inland Waters, Environment Canada, Burlington, Ont.

Howell, G., 1984. Compliance of Selected Water Quality Parameters to the Objectives of the International Waters of the Saint John River Basin During the Years 1982 and 1983. Tech. Rep. IWD-AR-WQB-84-56, Water Quality Branch, Environment Canada, Moncton, N.B.

Howell, G., L. Wong, J. Fenton and R. Bingham, 1985. NABIODAT, The Biological Data Management System. Tech. Rep. IWD-AR-WQB-85-90, Water Quality Branch, Environment Canada, Moncton, N.B.

Howell, G., 1986. Water Quality Characterization of 78 Acid Precipitation Monitoring Lakes in Atlantic Canada. Tech. Rep. IWD-AR-WQB-86-109, Water Quality Branch, Environment Canada, Moncton, N.B.

ITAS, 1980. Review and Update of Water Quality Objectives for the International Waters of the Saint John River Basin. A Report of the International Technical Advisory Subcommittee on Water Quality in the Saint John River Basin.

King, D.E., 1982. Credibility: The Consequences of Quality Assurance. Laboratory Services Branch, Ontario Ministry of the Environment.

Leenheer, J.A. and T.I. Noyes, 1984. A Filtration and Column Adsorption System for On site Concentration and Fractionation of Organic Substances from Large Volumes of Water. U.S. Geological Survey Water-Supply Paper 2230, Washington.

Likens, G.F., F.H. Bormann and J.S. Eaton, 1980. Variations in Precipitation and Streamflow Chemistry at the Hubbard Brook Experimental Forest During 1964 to 1977. In Effects of Acid Precipitation on Terrestrial Ecosystems, Eds. T.C. Hutchinson and M. Haros, Plenium Press, New York.

Lockerbie, D., 1981. Quality Assurance in the Atlantic Region. Proceedings of the Field Quality Assurance Workshop. Water Quality Branch, Environment Canada, Burlington, Ont.

Lockerbie, D., 1987. Compliance of Selected Water Quality Parameters to the Objectives of the International Waters of the Saint John River Basin During the Years 1984 and 1985. Tech. Report IW/L-AR-WQB-87-118, Water Quality Branch, Environment Canada, Moncton, N. B.

Miller, R.G., J.V. Doerger, F.C. Kopfler, J. Stober and P. Roberson, 1985. Anal. Chem., 57:1020.

O'Neill, H.J. and H.S. Bailey, in prep. Off-Target Fallout of the Insecticide Fenitrothion and Aminocarb During the Spruce Budworm Spray Program in New Brunswick, 1980-1983. Water Quality Branch, Environment Canada, Moncton, N.B.

Ongley, E.D., D.A. Birkholy, J. Carey and M.R. Samoiloff, 1986. Is Water a Relevant Sampling Medium for Toxic Chemicals?: An Alternative Environmental Sensing Strategy. National Water Research Institute Contribution #86-24, Burlington, Ont.

Sandberg, D.K., N.R. McQuaker, R.J. Vet and H.A. Weibe, 1986. Snowpack: Recommended Methods for Sampling and Site Selection. Federal/Provincial Research and Monitoring Coordinating Committee, Quality Assurance Subgroup, Downsview, Ontario.

Taylor, J.K. and T.W. Stanley, 1985. Quality Assurance for Environmental Measurements. ASTM Special Tech. Publ. 867, Philadelphia, Pa.

Wong, L., R. Bingham and T. LeBlanc, 1984. LABS-11 - Users Manual VAX 11 750 Version. Tech. Report IWD-AR-WQB-85-71, Water Quality Branch, Environment Canada, Moncton, N.B.

Woodrow, J.E., M.S. Majewski and J.N. Seiber, 1986. Environ. Sci. Health, B21(2):143.

Work Group (Ad-Hoc) on Quality Control, 1983. Guidelines for In-lab Quality Control for LRTAP Projects. A report presented to the LRTAP Quality Assurance and Methods Subgroup of the Federal-Provincial Research Monitoring and Coordinating Committee.

WQB-AR, 1982. LABS-11 - A Laboratory Data Management System. Water Quality Branch, Environment Canada, Moncton, N.B.

WQB, 1981. Analytical Methods Manual. Water Quality Branch, Environment Canada, Ottawa.

WQB, 1983. Sampling for Water Quality. Water Quality Branch, Environment Canada, Ottawa.

WQB, 1986. NAQUADAT Dictionary of Parameter Codes. Water Quality Branch, Environment Canada, Ottawa.